(12) UK Patent Application (19) GB (11) 2 325 885 (13) A

(43) Date of A Publication 09.12.1998

(21) Application No 9811828.4

(22) Date of Filing 03.06.1998

(30) Priority Data
(31) 9711383 (32) 03.06.1997 (33) GB

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(51) INT CL[6]
B41C 1/10, B41N 3/03

(52) UK CL (Edition P)
B6C CHB C602 C630 C631 C636 C644
G2C CHX CH6B4 CH6C2 CH6C4 CH6D2

(56) Documents Cited
GB 1402760 A EP 0816071 A EP 0628409
EP 0609941 A US 5632204 A

(58) Field of Search
UK CL (Edition P) B6C CHB CHD, G2C CA4G CHX
INT CL[6] B41C, B41N, G03F

(54) Abstract Title
Printing plates

(57) A lithographic printing plate precursor comprises a grained and anodised aluminium substrate coated with a metallic layer, preferably a silver layer, on top of which is applied a transparent cover sheet or layer of material. Imagewise exposure of the precursor by means of a high intensity laser beam allows for the direct provision of press ready plates showing high image quality, good press properties and high durability on press without the requirement for the use of intermediate film and developer chemistry. The transparent cover sheet or layer of material enables the loosely bound debris which is produced in the exposed areas on imagewise exposure to be trapped, and thereby prevented from being released to the atmosphere. Specified sheets are polyolefines and polyethylene terephthalate and specified layers are polyvinyl alcohol, polyvinyl phosphonic acid, polyethylene glycol, gum arabic and carboxymethylcellulose.

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HEAT SENSITIVE PRINTING PLATE PRECURSORS

This invention relates to the formation of images directly from electronically composed digital sources and is particularly concerned with the formation of images on lithographic printing plate precursors. More particularly, the invention relates to lithographic printing plate precursors which incorporate an imaging layer comprising metallic silver, and a method of preparing lithographic printing plates which does not require the use of chemical treatments.

Lithographic printing is a process of printing from surfaces which have been prepared in such a way that certain areas are capable of accepting ink (oleophilic areas), whereas other areas will not accept ink (oleophobic areas). The oleophilic areas form the printing areas while the oleophobic areas form the background areas.

Plates for use in lithographic printing processes may be prepared using a photographic material that is made imagewise receptive or repellent to ink upon photo-exposure of the photographic material and subsequent chemical treatment. However, this method of preparation, which is based on photographic processing techniques, involves several steps, and therefore requires a considerable amount of time, effort and expense.

Consequently it has, for many years, been a long term aim in the printing industry to form images directly from an electronically composed digital database, ie by a so-called "computer-to-plate" system. The advantages of such a system over the traditional methods of making printing plates are:

(i) the elimination of costly intermediate silver film and processing chemicals;
(ii) a saving of time; and
(iii) the ability to automate the system with consequent reduction in labour costs.

The introduction of laser technology provided the first opportunity to form an image directly on a printing plate precursor by scanning a laser beam across the surface of the precursor and modulating the beam so as to effectively turn it on and off. In this way, radiation sensitive plates comprising a high sensitivity polymer coating have been exposed to laser beams produced by water cooled UV argon-ion lasers and electrophotographic plates having sensitivities stretching into the visible spectral region have been successfully exposed using low powered air-cooled argon-ion, helium-neon and semiconductor laser devices.

Imaging systems are also available which involve a sandwich structure which, on exposure to a heat generating infra-red laser beam, undergoes selective (imagewise) delamination and subsequent transfer of materials. Such so-called peel-apart systems are generally used as replacements for silver halide films.

A digital imaging technique has been described in US Patent No 4911075 whereby a so-called driographic plate which does not require dampening with an aqueous fountain solution to wet the non-image areas during printing is produced by means of a spark discharge. In this case, a plate precursor comprising an ink-repellent coating containing electrically conductive particles coated on a conductive substrate is used and the coating is ablatively removed from the substrate. Unfortunately, however, the ablative spark discharge provides images having relatively poor resolution.

It is known to improve this feature by the use of lasers to obtain high resolution ablation as described, for example, by P E Dyer in "Laser Ablation of Polymers" (Chapter 14 of "Photochemical Processing of Electronic Materials", Academic Press, 1992, p359-385). Until recently, imaging via this method generally involved the use of high power carbon dioxide or excimer lasers. Unfortunately, such lasers are not well-suited to printing applications because of their high power consumption and excessive cost, and the requirement for high pressure gas handling systems. Recent developments have, however, led to the availability of more suitable infra-red diode lasers, which are compact, highly efficient and very economical solid state devices.

High power versions of such lasers, which are capable of delivering up to 3000 mJ/cm^2, are now commercially available.

Coatings which may be imaged by means of ablation with infra-red radiation have previously been proposed. Thus, for example, a proofing film in which an image is formed by imagewise ablation of a coloured layer on to a receiver sheet is described in PCT Application No 90/12342. This system is, however, disadvantageous in requiring a physical transfer of material in the imaging step, and such methods tend to give rise to inferior image resolution.

Much superior resolution is obtained by means of the ablation technique described in European Patent No 649374, wherein a driographic printing plate precursor is imaged digitally by means of an infra-red diode laser or a YAG laser, and the image is formed directly through the elimination of unwanted material. The technique involves exposing a plate precursor, incorporating an infra-red radiation ablatable coating covered with a transparent cover sheet, by directing the beam from an infra-red laser at sequential areas of the coating so that the coating ablates and loses its ink repellancy in those areas to form an image, removing the cover sheet and ablation products, and inking the image.

A heat mode recording material is disclosed in US Patent No 4034183 which comprises an anodised aluminium support coated with a hydrophilic layer. On imagewise exposure using a laser, the exposed areas are rendered hydrophobic, and thereby accept ink.

Japanese patent application laid open to public inspection No 49-117102 (1974) discloses a method for producing printing plates wherein a metal is incorporated in the imaging layer of a printing plate precursor which is imaged by irradiation with a laser beam modulated by electric signals. Typically, the plate precursor comprises a metal base, such as aluminium, coated with a resin film, which is typically nitrocellulose, and on top of which has been provided a thin layer of copper. The

resin and metal layers are removed in the laser-struck areas, thereby producing a printing plate. The disadvantage of this system, however, is that two types of laser beam irradiation are required in order to remove firstly the copper (eg by means of an argon-ion laser) and then the resin (eg with a carbon dioxide laser); hence, the necessary equipment is expensive.

Subsequently a method of printing plate production which obviated the requirement for a second laser exposure was disclosed in Japanese patent application laid open to public inspection No 52-37104 (1977). Thus, a printing plate precursor comprising a support, typically aluminium, an anodic aluminium oxide layer, and a layer of brass, silver, graphite or, preferably, copper is exposed to a laser beam of high energy density in order to render the exposed areas hydrophilic to yield a printing plate. The printing plate precursor is, however, of rather low sensitivity and requires the use of a high energy laser for exposure.

An alternative heat mode recording material for making a lithographic printing plate is disclosed in European Patent No 609941, which comprises a support having a hydrophilic surface, or provided with a hydrophilic layer, on which is coated a metallic layer, on top of which is a hydrophobic layer having a thickness of less than 50nm. A lithographic printing plate may be produced from the said material by imagewise exposing to actinic radiation, thereby rendering the exposed areas hydrophilic and repellent to greasy ink.

Conversely, European Patent No 628409 discloses a heat mode recording material for making a lithographic printing plate which comprises a support and a metallic layer, on top of which is provided a hydrophilic layer having a thickness of less than 50nm. A lithographic printing plate is produced by imagewise exposing the material to actinic radiation in order to render the exposed areas hydrophobic and receptive to greasy ink.

In each of the two foregoing heat mode recording materials, however, difficulties in printing will be encountered. On exposure of the materials to actinic radiation, the energy is converted to heat in the image areas by interaction with the metallic layer, thereby destroying the hydrophilicity or hydrophobicity - depending on the material employed - of the topmost layer in those areas. Consequently, the surface of the metallic layer becomes exposed, and the success of the printing operation is dependent upon differences in hydrophilicity and oleophilicity between the metallic surface and the hydrophilic or hydrophobic layer, as the case may be. Since the metallic layer functions as the hydrophobic surface in one case, and as the hydrophilic surface in the alternative case, it would be expected that such differences in hydrophilicity and oleophilicity would not be sufficiently clearly defined so as to provide a satisfactory printing surface. Furthermore, when a hydrophilic layer is present, and the metallic surface functions as the oleophilic areas of the plate, image areas will necessarily be printed from the metallic surface; such an arrangement is known to be unsatisfactory, and to result in difficulties in achieving acceptable printing quality.

It is an object of the present invention to provide a lithographic printing plate having excellent printing properties, and a method of making said plate which obviates the requirement for the use of processing developers after exposure.

It is a further object of the present invention to provide a method of preparing a lithographic printing plate which does not require the use of costly intermediate film and relies on direct-to-plate exposure techniques.

It is a still further object of the present invention to provide a method of producing a lithographic printing plate in which a high quality image results from the ablation of a metallic layer from a hydrophilic support, thus providing a high degree of differentiation between hydrophilic and oleophilic areas.

It is an additional objective of the present invention to provide a method of producing a lithographic printing plate according to the previous objectives, wherein the ablated materials which are formed during exposure may be efficiently collected and removed without presenting a hazard to the user or the environment.

According to a first aspect of the present invention there is provided a lithographic printing plate precursor comprising:

(i) a grained and anodised aluminium substrate, having coated thereon
(ii) a metallic layer, on top of which is applied
(iii) a transparent cover sheet or layer of material.

The substrate employed in the present invention is an aluminium substrate which has been electrochemically grained and anodised on at least one surface in order to enhance its lithographic properties. Optionally, the aluminium may be laminated to other materials, such as paper or various plastics materials, in order to enhance its flexibility, whilst retaining the good dimensional stability associated with aluminium.

The metallic layer, which is applied to the grained and anodised surface of the aluminium, may comprise any of several metals, specific examples of which include copper, bismuth and brass. Most preferably, however, the metallic layer comprises a silver layer. The thickness of the metallic layer is preferably from 20 nm to 200 nm, most preferably from 40 nm to 100 nm

Various techniques are available for the application of the metallic layer to the grained and anodised aluminium substrate, including vapour or vacuum deposition or sputtering. In the case where the metal layer comprises a silver layer, however, the most preferred method for applying the layer involves the treatment of a silver halide photographic material according to the silver salt diffusion transfer process.

In the diffusion transfer process, a silver halide emulsion layer is transformed by treatment with a so-called silver halide solvent, into soluble silver complex compounds which are then allowed to diffuse into an image receiving layer and are reduced therein by means of a developing agent, generally in the presence of physical development nuclei, to form a metallic silver layer.

Two such systems are available: a two sheet system in which a silver halide emulsion layer is provided on one element, and a physical development nuclei layer is provided on a second element, the two elements are placed in contact in the presence of developing agent(s) and silver halide solvent(s) in the presence of an alkaline processing liquid, and subsequently peeled apart to provide a metallic silver layer on the second element; and a single sheet system wherein the element is provided with a physical development nuclei layer, a silver halide emulsion layer is provided on top thereof, the element is treated with developing agent(s) and silver halide solvent(s) in the presence of an alkaline processing liquid, and the element is washed to remove spent emulsion layer and leave a metallic silver layer which is formed in the layer containing physical development nuclei.

Alternatively, the diffusion transfer process may be used to apply a metallic silver layer by overall exposing a positive working silver halide emulsion layer to form a latent negative image which is then developed in contact with a physical development nuclei layer to form a metallic silver layer. Again, the process may be carried out using either a single sheet or a double sheet system.

The principles of the silver complex diffusion transfer process are fully described in the publication "Photographic Silver Halide Diffusion Processes" by Andre Rott and Edith Weyde, The Focal Press, London and New York, 1972, and further detail may be gleaned by reference thereto.

The transparent cover sheet or layer of material which is applied over the metallic layer allows the loosely bound debris which is produced in the image areas on

exposure to be trapped and, thus, be prevented from being released to the atmosphere. Thus, the method of producing a lithographic plate is made simpler and more efficient, since all the chemical products generated on exposure are contained on, or within, the cover sheet or layer and will not, therefore, present a hazard to the user or the environment; additionally, the possibility of damage being caused to the imaging exposure equipment is prevented.

The cover sheet or layer of the invention may be applied by covering the plate with a pre-formed sheet of a film material or, alternatively, by coating the plate with a top layer of a film-forming material which remains on the plate after exposure.

A cover sheet or a pre-formed film may be comprised of any suitable film material which is transparent to infra-red radiation, for example, polyethylene, polypropylene, poly(ethylene terephthalate) or a masking film having a structure and composition as described in EP-A-323880. Optionally, an adhesive layer may be present between the cover sheet and the metallic layer.

A coated top layer of infra-red transparent material may be applied from aqueous or organic solvent solution, but preferably from aqueous solution and may comprise materials such as poly(vinyl alcohol), poly(ethylene glycol), poly(vinyl phosphonic acid), gum arabic, carboxymethyl cellulose, but preferably the material of the layer should be easily removed by aqueous washing. Optionally, other chemicals can be added to the coating such as may enhance the press performance of the printing plate. Such other chemicals may comprise a proteolytic enzyme, a silver oleophilising compound such as disclosed on pages 105 to 106 of "Photographic Silver Halide Diffusion Processes" by Andre Rott and Edith Weyde, with mercapto compounds being particularly preferred, and compounds selected to buffer the coating to a given pH.

Following imagewise exposure of the lithographic printing plate precursor prepared with a cover sheet, the cover sheet may be conveniently removed by peeling away

from the surface of the plate to leave an imaged, press ready printing plate. The cover sheet containing the entrapped ablation debris may then be disposed of in a safe manner.

Following imagewise exposure of the lithographic printing plate precursor prepared with a coated top layer, the coated layer may be removed by physically rubbing with a cloth or scrubbing either manually or automatically with a wet brush or plush fabric. Alternatively, the plate may be mounted on the press such that removal of the coated layer, together with the ablation debris, occurs as a result of the action of the press fount solutions or other press start-up chemicals or procedures that are used in the course of normal printing operations. In this case it is preferable that the material of the coated layer is easily removed from the plate surface by the action of the press.

The thickness of the cover sheet may be up to 200 μm, preferably from 20 μm to 100 μm. The coated top layer can be applied to give a dry coating weight of between 0.5 and 10 g/m^2, preferably between 2 and 6 g/m^2

According to a second aspect of the present invention, there is provided a method of preparing a lithographic printing plate, said method comprising:

a) providing a lithographic printing plate precursor as hereinbefore described;
b) imagewise exposing said precursor by means of a high intensity laser beam; and
c) removing the transparent cover sheet or layer.

In order to prepare a lithographic printing plate, the precursor is imaged by a beam of radiation, preferably from a laser operating in the infra-red region of the spectrum. Examples of suitable infra-red lasers include semiconductor lasers and YAG lasers, for example the Gerber Crescent 42T Platesetter with a 10 W YAG laser outputting at 1064 nm. Exposure to the beam of radiation causes ablation of the metallic layer to occur in the radiation-struck areas.

Following exposure and removal of the cover sheet, or washing-off of the coated top coat, together with the ablated debris, the plate is preferably prepared for printing operations by treatment with a composition comprising a proteolytic enzyme, a silver oleophilising agent and a desensitising compound. In this way, it is possible to ensure good ink acceptance in image areas and a high degree of hydrophilicity in background areas, thus enabling a good start-up on press to be achieved. However, if the coated top coat is intended to be removed on press, then no further treatment is required at this stage.

Suitable enzymes for use in the above composition may include, for example, trypsin, pepsin, ficin, papain or the bacterial proteases or proteinases. Oleophilising compounds may be chosen from those disclosed on pages 105 to 106 of "Photographic Silver Halide Diffusion Processes" by Andre Rott and Edith Weyde, but mercapto compounds and cationic surfactants such as quaternary ammonium compounds are of particular value. Carbohydrates such as gum arabic, dextrin and inorganic polyphosphates such as sodium hexametaphosphate provide useful desensitising compounds in these compositions.

Typically, the compositions comprise aqueous solutions containing from 0.1% to 10.0% by weight of enzyme, from 0.05% to 5.0% by weight of oleophilising compound and from 1.0% to 10.0% by weight of desensitising compound.

The method of the present invention provides press ready plates showing high image quality, good press properties and high durability on press without the requirement for the use of costly intermediate film and developer chemistry and the attendant inconvenience resulting from the use of these materials.

The following example is illustrative of the invention, without placing any limit on the scope thereof:

EXAMPLES

Example 1

A commercially available Howson SILVERLITH® SDB printing plate, available from Agfa-Gevaert Ltd., was processed without exposure through an automatic processor by means of the diffusion transfer reversal method, in accordance with the recommendation of the manufacturer, but the final stage of applying a specified finishing gum was omitted. The resulting printing plate precursor comprised a grained and anodised aluminium substrate, on the anodised surface of which was coated a layer of silver.

A sheet of polyethylene (supplied by Samuel Grant Ltd, Leeds, UK), having a thickness of 50 μm, coated on one side with a silicone release adhesive, was firmly applied to the layer of silver on the printing plate precursor to give a well adhered covering over the plate surface.

The assembly was then loaded onto a Gerber Crescent 42T internal drum Laser Platesetter fitted with an extraction system containing a nozzle about 1cm away from the plate surface and an air suction pump connected to the nozzle by flexible ducting. An air sampling port was provided on the exhaust side of the pump. The plate precursor was imagewise exposed to a 10 W YAG laser outputting at a wavelength of 1064 nm and peak power density of 6.5 MW/cm^2. The cover sheet was then removed to reveal the anodic oxide layer of the lithographic substrate in the areas where the laser beam had impinged, and the residual debris formed during exposure was retained on the cover sheet. No adverse effects from volatile debris were observed.

After removal of the cover sheet, the surface of the printing plate was treated with an aqueous solution comprising a proteolytic enzyme, an oleophilising agent and a desensitising gum prior to mounting on a printing press. This treatment ensured a good start-up to printing operations with image areas showing high oleophilicity with good ink acceptance, and background non-image areas being clean and free from ink

adhesion. The plate produced 80,000 good quality copies on a Drent Web Offset printing press.

As a control a lithographic printing plate precursor was prepared in identical fashion, except that no cover sheet was applied. On exposure, the ablated material which was released into the atmosphere created a highly unpleasant odour.

Example 2

A Howson SILVERLITH® printing plate was processed according to example 1 but in this case a cover sheet was not applied and, as an alternative, a range of coatings was applied to the silver layer of the printing plate precursor by means of a wire bar. After application the coated layers were dried and the plate assembly was loaded on a Gerber Crescent 42T Platesetter and imagewise exposed as in example 1. The thus exposed plates were taken off the Platesetter and either mounted on a press cylinder without any further treatment or the coated top coat was removed by passing through the re-entry section of the automatic plate processor used to make the printing plate precursor in example 1. This section comprised a plush covered roller onto which water was sprayed to effectively remove the top coat. Finisher was then conventionally applied to the plate by the processor as it passed from the re-entry section into the finisher section. The plates were then mounted on the press.

Various coating weights of top coat were applied to help demonstrate the invention. The effectiveness of the top coat in containing ablation was measured by standard analytical air sampling methods and also by assessing the degree of odour that could be smelt in the exhaust air. The results are summarised in Table 1.

When a topcoat of coat weight of about 2 g/m^2 was applied to the silver layer of the printing plate, significant suppression of airborne ablation products was demonstrated. Complete elimination of airborne ablation products was only achieved when a top coat with coat weight of at least 4 g/m^2 was coated onto the silver layer of the printing plate. All the given examples performed successfully on a printing press.

Top Coat Composition	Coat Weight (g/m^2)	Air Sampling (ppm silver in air exhaust)	Smell Detected
None		20	yes
Standard finisher[1]	0.3	20	yes
Standard finisher[1]	4.0	5	faint
Poly(vinyl alcohol)[2]	2.5	2	faint
Poly(vinyl alcohol)[2]	4.5	none detected	no
Carboset® 525[3]	4.0	none detected	no
Poly(vinyl phosphonic acid)[4]	2.3	8	yes
Poly(vinyl phosphonic acid)[4]	4.1	none detected	no
Poly(vinyl phosphonic acid) + Alcalase® 2.5L + OMT + triethanolamine to pH 7[5]	4.1	none detected	no
Gum arabic	2.0	10	yes
Gum arabic	5.2	none detected	no

TABLE 1

1. Standard finisher recommended by the manufacturers: comprises sodium hexametaphosphate, 1-octyl-5-mercapto-1,2,3,4-tetrazole, an enzyme (Alcalase 2.5L), and buffering agents to give pH 7.

2. 10-23K mol wt; 88% hydrolysed; coated from 10% aqueous solution.

3. Commercial alkali soluble acrylic co-polymer coated from 10% aqueous ammoniacal solution.

4. 10K mol wt; coated from 20% aqueous solution.

5. Alcalase® 2.5L is a commercial enzyme; OMT = 1-octyl-5-mercapto-1,2,3,4-tetrazole; triethanolamine acts as a buffer.

CLAIMS

1. A lithographic printing plate precursor comprising:

   (i) a grained and anodised aluminium substrate having coated thereon
   (ii) a metallic layer on top of which is applied
   (iii) a transparent cover sheet or layer of material.

2. A lithographic printing plate precursor as defined in claim 1 wherein said metallic layer comprises a silver layer.

3. A lithographic printing plate precursor as defined in claim 2 wherein said silver layer is applied by means of the silver salt diffusion transfer process.

4. A lithographic printing plate precursor as defined in claim 1, 2 or 3 wherein said metallic layer has a thickness of from 20 nm to 200 nm.

5. A lithographic printing plate precursor as defined in claims 1-4 wherein said transparent cover sheet or layer of material comprises a sheet of film material which is transparent to infra-red radiation.

6. A lithographic printing plate precursor as defined in claim 5 wherein said film material comprises polyethylene, polypropylene or poly(ethylene terephthalate).

7. A lithographic printing plate precursor as defined in claims 1-4 wherein said transparent cover sheet or layer of material comprises a coated layer of material which is applied from aqueous or organic solvent solution.

8. A lithographic printing plate precursor as defined in claim 7 wherein said material comprises poly(vinyl alcohol), gum arabic, poly(vinyl phosphonic acid), carboxymethylcellulose or poly(ethylene glycol).

9. A lithographic printing plate precursor as defined in claim 5 or 6 wherein said sheet of film material has a thickness of up to 200μm.

10. A lithographic printing plate precursor as defined in claim 7 or 8 wherein said coated layer of material has a dry coating weight of between 0.5 g/m^2 and 10 g/m^2.

11. A method of preparing a lithographic printing plate, said method comprising :

(a) providing a lithographic printing plate precursor as defined in any of claims 1-10 ;
(b) imagewise exposing said precursor by means of a high intensity laser beam; and
(c) removing the transparent cover sheet or layer.

12. A method as defined in claim 11 wherein said transparent cover sheet or layer is removed by peeling away from the surface of the plate following imagewise exposure.

13. A method as defined in Claim 11 wherein said transparent cover sheet or layer is removed by physical means of rubbing or scrubbing.

14. A method as defined in claim 11 wherein said transparent cover sheet or layer is removed by the action of a press fount solution during printing operations.

15. A lithographic printing plate precursor as defined in Claim 1 substantially as herein described with reference to the accompanying examples.

16. A method of preparing a lithographic printing plate as defined in Claim 11 substantially as herein described with reference to the accompanying examples.

17. A lithographic printing plate when produced by the process of Claim 11.

The Patent Office

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Application No: GB 9811828.4
Claims searched: 1-17

Examiner: Meredith Reynolds
Date of search: 25 August 1998

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): B6C (CHB,CHD), G2C (CHX, CA4G)

Int Cl (Ed.6): B41C 1/10,1/055, B41N 3/03, G03F 7/06

Other:

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	GB 1402760	(ECD)(pp 6-10, Exs)	1,4,7-8,10
X,P	EP 0816071A	(Agfa)(Col 8 lines 36-48, Col 9 lines 1-5, Exs)	1,4,7,11, 13,17
X	EP 0628409A	(Agfa)(Ex 2, p4 lines 37-41)	1-4,7-8, 11,13,17
X	EP 0609941A	("")(Ex 2, p 5 lines 32-36)	1-4,7-8, 11,13,17
X	US 5632204	(Presstek)(whole doc, esp. Cols 4-5)	1,4,7-8, 10-11,17

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
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